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Lyotropic Phases of Dodecylbenzenesulfonates with Different Counterions in Water

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The lyotropic phase behavior of (technical grade) dodecylbenzenesulfonates (DoBS) is strongly influenced by the type of counterion and the relative amount of water. Phase diagrams are composed for the following systems: HDoBS/water, NaDoBS/water, (HDoBS + NaDoBS 1:1)/water, LiDoBS/water, KDoBS/water, CsDoBS/water, $Ca(DoBS)_2$/water, NaDoBS/water/NaCl, and NaDoBS/water/CsCl. The phases were characterized by light microscopy, freeze-fracture electron microscopy, X-ray diffraction, and macroscopic appearance. The phase diagrams all contain large areas of lamellar phases. The appearance of the lamellar phases differs along this series, in particular regarding swelling behavior, either with or without a micellar phase next to the lamellar phase, and formation of large, rather irregular lamellar units versus smaller, perfectly spherical lamellar topologies (so-called lamellar droplets). LiDoBS shows, in addition, a hexagonal phase between 25 and 50 wt %. Explanations for the occurrence of the different phases are given in molecular terms and in terms of interactions between bilayers and between aggregates.

Introduction

The class of alkylarenesulfonates is the most widely used surfactant for detergent products worldwide.[1−5] Despite its commercial importance, only little is known about the lyotropic phase behavior of these types of compounds in water.[6] Tiddy and co-workers[7] reported a partial phase diagram of the isomerically pure sodium dodecyl-5-p-benzenesulfonate. In contrast, a large body of phase diagrams of many other amphiphiles is known.[6,8−10] We are interested in the phase diagrams of the lyotropic liquid-crystalline phases of (polydisperse) dodecylbenzenesulfonates (DoBS) with several different counterions. This interest has been inspired by our research aimed at finding out how surfactant molecules obtain a lamellar arrangement. More specifically the dynamic process of the formation of the lamellar phase is examined starting from a less ordered system such as the micellar phase or the isotropic bulk surfactant.[11] The lamellar arrangement of surfactant molecules finds an important commercial application in several liquid laundry detergents and household cleaning products,[12] where the lamellar units (so-called lamellar droplets) are homogeneously dispersed in the product.

Previously we have studied how a lamellar arrangement of surfactant molecules can be obtained by the addition of salt to a dilute micellar solution of sodium dodecylbenzenesulfonate (NaDoBS) or a mixture of NaDoBS and a nonionic surfactant (a poly(ethylene glycol) alkyl monoether, $C_{13-15}E_{\langle 7\rangle}$) in water.[13,14] More closely related to the processing of commercial products is a study toward the formation of the lamellar phase starting from the bulk surfactant. In the case of dodecylbenzenesulfonates the industrial precursor for commercial products usually is the acidic form (HDoBS), which is an isotropic liquid. Important steps in the manufacturing of a commercial product are the neutralization of this acid by (sodium) hydroxide and the penetration of water into the bulk surfactant. Moreover, the presence of extra salt in the aqueous phase strongly influences the appearance of the lamellar phase. If one wants to know how a surfactant molecule adopts a lamellar arrangement in the presence of the other ingredients that are present in commercial products, its aggregation behavior should be followed from the bulk surfactant state to the state of lamellar arrangement. In order to do so, first insight ought to be obtained at which compositions the lamellar arrangement occurs and what are the environmental requirements for a lamellar arrangement. In other words, the surfactant/water/salt phase diagram needs to be examined. The problem asks for a four-component phase diagram: water/HDoBS/NaOH/NaCl, as depicted in Figure 1. The most

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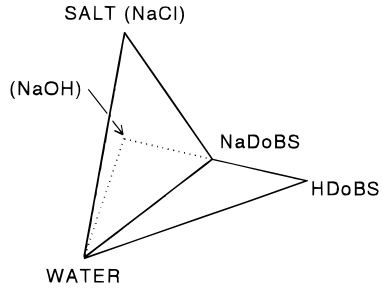


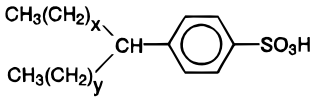
Figure 1. Schematic drawing of the four-component water/ HDoBS/NaOH/ NaCl phase diagram.

important part of this diagram is the right-hand half of the base of this trigonal pyramid. Halfway along the HDoBS/NaOH axis lies NaDoBS (formally this is NaDoBS + H_2O 1:1).

The lyotropic phase behavior along the HDoBS/water axis appeared to differ remarkably from the phase behavior observed on the NaDoBS/water line. To understand the difference in phase behavior between DoBS with either H_3O^+ or Na^+ as the counterion, other counterions have been studied as well: Li^+, K^+, Cs^+, and Ca^{2+}. A large variation in phase behavior can be traced back to the hydration characteristics of the cations.[15,16] Several other systems are known where the lyotropic phase behavior varies with the type of counterion.[8,17−22] Once the phase diagrams are known, these can be used to trace out the route from the bulk surfactant phase toward the lamellar phase. This will be the topic of a following paper.[23] We also have studied the process of penetration of water into bulk surfactant using the cryo-transmission electron microscopy technique.[24]

Experimental Section

Materials. Technical dodecylbenzenesulfonic acid (HDoBS, "MARLON AS3", Hüls, 96.7% pure, provided by Unilever Research Laboratory, Vlaardingen, The Netherlands) has an average composition as sketched below. It contains 0.2% sulfuric



$x + y = 8.4$

acid and 1.7% non-surface-active organic material, the remaining part being water. Residual water has been removed from HDoBS by azeotropic distillation of toluene, followed by prolonged vacuum treatment at elevated temperature to remove the remaining toluene. No traces of toluene were found by NMR (^{1}H-NMR in $CDCl_3$ solution, recorded on a 200 MHz Varian Gemini 200). NaDoBS was prepared by reaction of HDoBS with sodium ethoxide in ethanol, followed by recrystallization from 2-propanol/ acetonitrile. Under these conditions, possibly a small fractionation has occurred (Elemental analysis $C_{17.4}H_{27.8}O_3SNa$ in weight percentage. Calculated: C, 61.5; H, 8.2; S, 9.4; Na, 6.8. Found: C, 61.7; H, 8.4; S, 9.5; Na, 7.3. The analysis is probably affected by the presence of trace amounts of Na_2SO_4.). LiDoBS, KDoBS, and CsDoBS were obtained by neutralization of HDoBS with LiOH, KOH, or CsOH, respectively, in anhydrous ethanol or acetone (KDoBS). LiDoBS appeared hard to crystallize. It was freeze-dried from water, yielding a waxy, yellow solid (Elemental analysis. LiDoBS: $C_{17.4}H_{27.8}O_3SLi$ (in weight percentage). Calculated: C, 64.5; H, 8.6; S, 9.9; Li, 2.1. Found: C, 62.9; H, 8.6; S, 9.5; Li, 2.0. KDoBS: $C_{17.4}H_{27.8}O_3S$. Calculated: C, 58.7; H, 7.8; S, 9.0; K, 11.0. Found: C, 58.6; H, 7.8; S, 9.0; K, 10.8. CsDoBS: $C_{17.3}H_{27.8}O_3SCs$. Calculated: C, 46.6; H, 5.9; S, 7.2; Cs, 29.6. Found: C, 44.1; H, 6.0; S, 6.7; Cs, 28.6). $Ca(DoBS)_2$ was prepared by Mr. Anno Wagenaar in our laboratory. HDoBS was neutralized with $Ca(acetate)_2$ in a 50 vol % ethanol/water mixture. The solvent was removed, and after stripping twice with dry ethanol, the product was crystallized from acetone, to obtain a white powder (Elemental analysis. $Ca(DoBS)_2$: $C_{34.6}H_{55.6}O_6S_2Ca$. Calculated: C, 62.0; H, 8.3; S, 9.5; Ca, 6.0. Found: C, 59.7; H, 8.2; S, 7.1; Ca, 4.6). The elemental analyses are probably affected by the hygroscopic nature of the compounds and by trace amounts of the corresponding sulfate salts, which might also have affected the position of the phase boundaries slightly.

Phase Diagrams. In order to construct the phase diagrams, samples were prepared by combining the appropriate amounts of amphiphile and water in small screw-capped vials, usually in steps of 10 wt % through the whole composition. In the regions where phase transitions occur, more sample compositions were studied. The phase boundaries are accurate within 3 wt % or less. The samples were homogenized by prolonged sonication, vigorous shaking, and temperature fluctuations. The samples were allowed to equilibrate for at least one week before characterization. The characterization was performed by light microscopy, using a Zeiss Axioplan or a Zeiss Axioskop light microscope. Some samples were examined by freeze-fracture electron microscopy, as described previously.[14] The temperature dependence of the phase transitions was first grossly determined by heating the samples in a water bath, increasing the temperature with increments of 10 °C, and allowing it to equilibrate for at least 1 h at a certain temperature, before observing the macroscopic appearance. The phase-transition temperatures were determined more accurately with a Nikon polarizing light microscope equipped with a Mettler FP82 hot stage, coupled to a Mettler FP80 processor, at the Netherlands Institute of Carbohydrate Research (NIKO-TNO) in Groningen, The Netherlands.

X-ray Measurements. Bilayer repeat distances were measured by X-ray using a Kratky compact small angle system (manufactured by Anton Paar, Austria), equipped with a position sensitive counter (manufactured by Braun, Germany). The camera was installed on a Philips PW1729 generator with a Cu anode X-ray tube ($\lambda = 0.1518$ nm). The generator was operated at 2 kW. The samples were sealed in 1 mm diameter Mark glass capillaries. The sample-to-counter distance was 200 mm.

Results

Phase diagrams will be presented that give an overview of the lyotropic phases of dodecylbenzenesulfonates with a variety of counterions and also in the presence of some salts. Two different single phases are usually separated by a two-phase area in the phase diagram, in compliance with the phase rule.[6,25] However, in some cases this two-phase area is too small to be indicated in the diagrams. Since all the amphiphiles must have a certain critical aggregation concentration, below which the amphiphile is dispersed only as monomers, all the phase diagrams should contain an area which represents such a solution of monomers. These are not indicated in the phase

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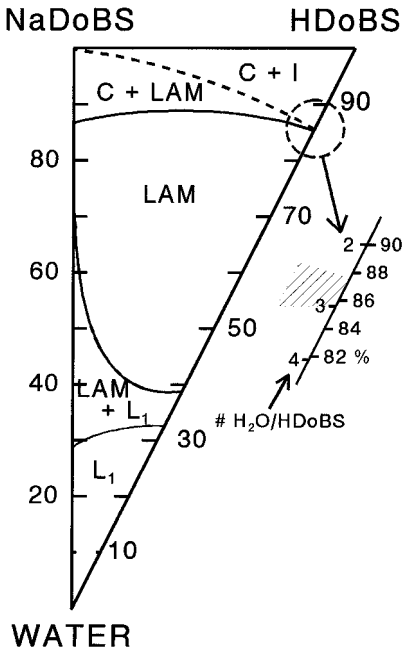

Figure 2. HDoBS/NaDoBS/water phase diagram at ambient temperature. I is the isotropic phase, LAM is the lamellar phase, and L_1 is the micellar phase.

diagrams, because these would fall practically on the *y*-axis of 100% water or electrolyte solution.

The HDoBS/NaDoBS/water phase diagram presented in Figure 2 is the right-hand half of the base of the multiple-component phase diagram shown in Figure 1. The starting point in the analysis of the phase behavior of dodecylbenzenesulfonates is the HDoBS corner of Figure 2. The first small amounts of water will mix homogeneously with the liquid HDoBS; water is dispersed as separate molecules in the isotropic phase (I). When the concentration of water molecules was increased to three water molecules per HDoBS molecule (86 wt % of HDoBS), enough water is present to display its directional properties: it forces the HDoBS to arrange itself into a lamellar fashion. This is also highlighted in Figure 2. At the transition a narrow two-phase lamellar plus isotropic area occurs, where stacks of lamellae appear as so-called bâtonnets.[6,26,27] Further increase of the water content leads to swelling of the lamellar phase (LAM), and accordingly the bilayer−bilayer distance will increase. This swelling continues to a composition of 39 wt % of HDoBS. At that point a micellar phase (L_1) appears next to the lamellar phase. Now the lamellar units appear again as bâtonnets. At 33 wt % HDoBS the lamellar phase has disappeared completely. Macroscopically, the micellar phase is recognized as a clear, somewhat viscous solution.

The most noteworthy difference on the NaDoBS/water line as compared to the behavior of the HDoBS/water system is the arrival in the two-phase micellar plus lamellar region already at 30 wt % water, 70 wt % NaDoBS. Further addition of water does not lead to swelling of the lamellar structure. Instead the water is used to facilitate the formation of micelles. At 29 wt % NaDoBS the lamellar phase has completely disappeared. To complete the diagram in Figure 2, the phase behavior was studied of a 1:1 mixture of HDoBS and NaDoBS in water at ambient temperature.

The difference between the swelling HDoBS lamellar phase and the nonswelling NaDoBS lamellar phase is apparent from the X-ray repeat distances (see below) and is also clearly seen by light microscopy (between crossed polars). The image of the 40 wt % HDoBS system (Figure 3A) is filled with a so-called mosaic texture. In contrast, the image of the 40 wt % NaDoBS system reveals irregularly shaped birefringent units in isotropic (micellar) surroundings. The lamellar character is also apparent from electron micrographs. Figure 4A shows a freeze-fracture electron microscopy (FFEM) micrograph of a focal conic domain, the structural unit of the mosaic structure that is seen by light microscopy (Figure 3A).[27−31] It can probably be considered the inverse of a lamellar droplet; if a lamellar droplet compares to an onion, the structural unit of the mosaic structure is a diabolo-like structure. In the FFEM image presented in Figure 4b, many (screw) dislocations can be seen in an 80 wt % HDoBS lamellar phase.[28,32]

The lyotropic-phase behavior of a 1:1 HDoBS/NaDoBS mixture is roughly comparable to the behavior of only HDoBS. Only at the concentrated end (90 wt % total surfactant) were crystals observed by light microscopy (not shown) amidst a continuous lamellar phase. Not surprisingly, it is easier for water to induce lamellar order in the HDoBS part than to break down the NaDoBS crystal structure.

Since the hydrophobic moiety and the headgroup are the same for HDoBS and NaDoBS, the difference in swelling behavior must be due to the difference in counterion: H^+ (or better H_3O^+) versus Na^+. In order to elaborate the role that the counterion plays in the lyotropic phase behavior of dodecylbenzensulfonates, different counterions were examined: Li^+, K^+, and Cs^+, with their different hydration characteristics, and Ca^{2+}, which strongly influences the electrostatic interactions. Summarized in Figure 5 are the lyotropic liquid-crystalline phases that occur at ambient temperature with these and earlier discussed counterions.

In many binary phase diagrams discussed in the literature a pronounced temperature dependence is seen. The lyotropic phases of dodecylbenzenesulfonates with alkali metal counterions also depend on the temperature. Only the lyotropic phases of the binary HDoBS/water and the $Ca(DoBS)_2$/water systems appeared to be hardly variant with temperature. Figure 6 displays four binary DoBS/water phase diagrams as a function of temperature.

NaDoBS. The phase boundaries in the NaDoBS/water system (Figure 6A) depend only slightly on temperature. Other details have been presented above. In NaDoBS/D_2O systems, lamellar units are already formed in a composition of 18.4 wt % NaDoBS/81.6 wt % D_2O, a system that contains a surfactant-to-solvent molecular ratio equal to the NaDoBS/H_2O ratio of a 20 wt % NaDoBS/80 wt % H_2O mixture, which is a *micellar* phase. It illustrates that D_2O has a lower capacity (a less negative Gibbs energy) for hydration of ionic species.[33]

LiDoBS. The lyotropic phase behavior of LiDoBS is characterized by the occurrence of a normal hexagonal phase at concentrations between 27 and 50 wt %. Macroscopically this is a clear gel. It has a well-defined appearance when viewed by light microscopy, as shown

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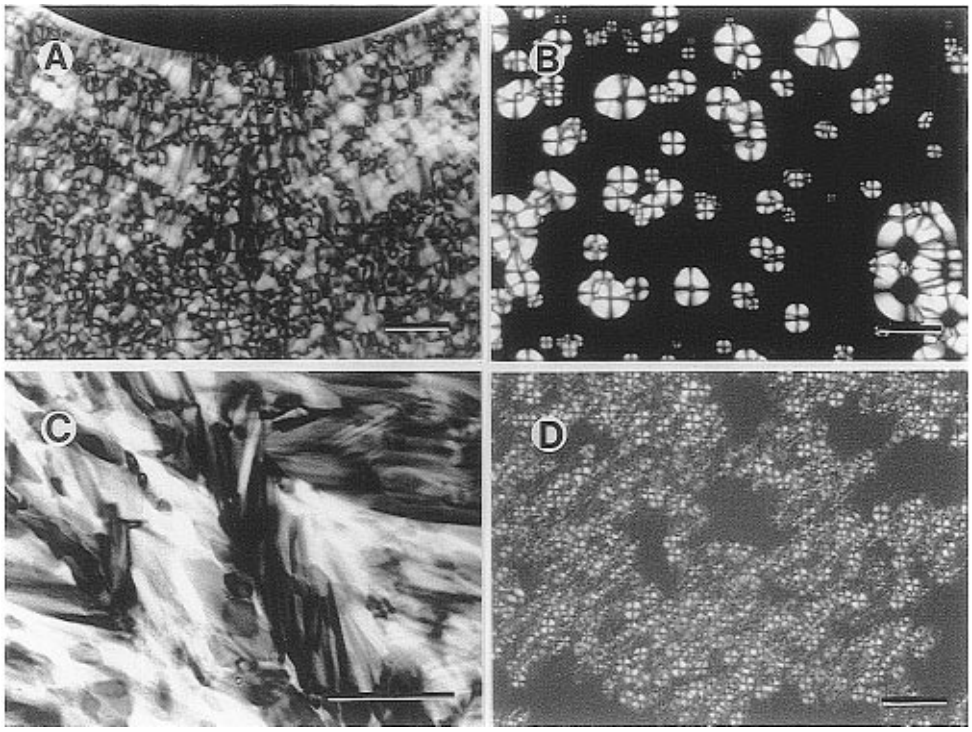

Figure 3. Light microscopy micrographs (between crossed polars) of several binary DoBS/water systems: (A) 40 wt % HDoBS one-phase continuous lamellar system; (B) 40 wt % NaDoBS, micellar phase and irregular shaped lamellar units; (C) 30 wt % LiDoBS one-phase hexagonal (H_1) system; (D) 30 wt % CsDoBS, dispersion of (mildly flocculated) lamellar droplets in a micellar phase. Bars represent 25 μm.

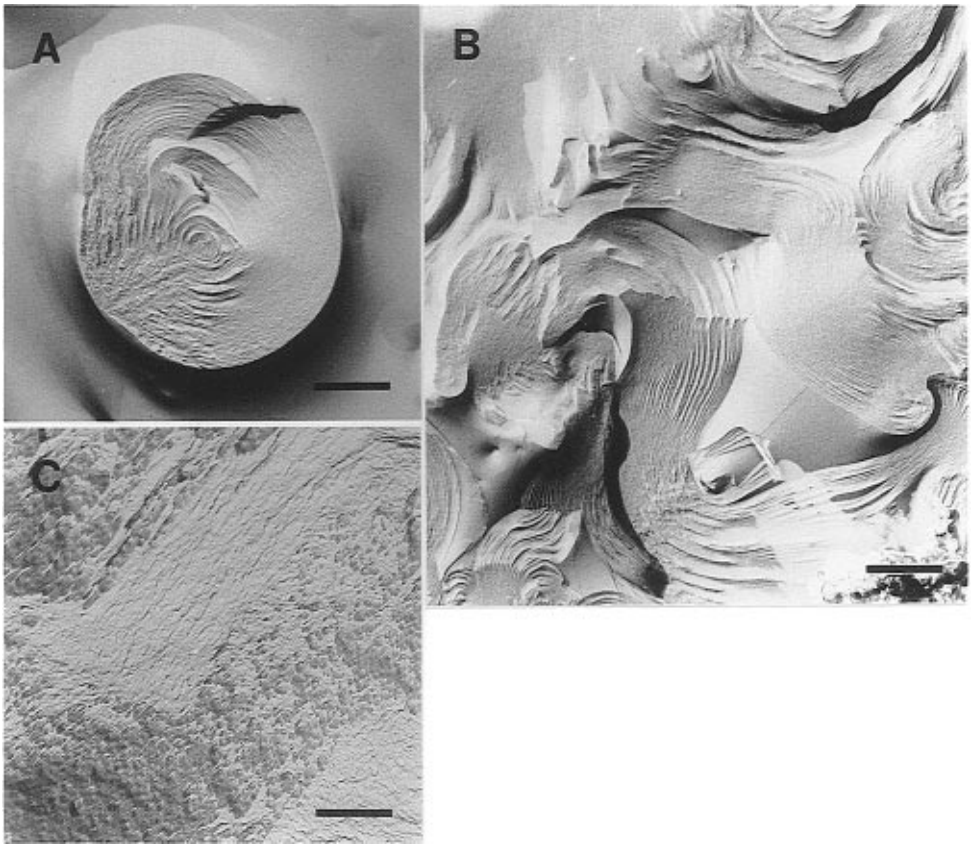

Figure 4. Freeze-fracture electron microscopy micrographs of (A) a focal conic domain in a 50 wt % HDoBS continuous lamellar phase; (B) several types of dislocations in an 80 wt % HDoBS continuous lamellar phase; and (C) the hexagonal phase of a 30 wt % LiDoBS system. Bars represent 500 nm.

in Figure 3C. Although more difficult to observe, the hexagonal character can also be seen by FFEM, as Figure 4C shows. In this cross-fracture the 60° ($1/3\pi$) angular positioning of the cylindrical units can even be inferred. Possibly, the fracturing process in a normal hexagonal phase leads to less contrast than that which occurs for the easily visible inverse hexagonal (H_{II}) phase.[34] A fracturing along the ribbons, as is common for the inverse hexagonal

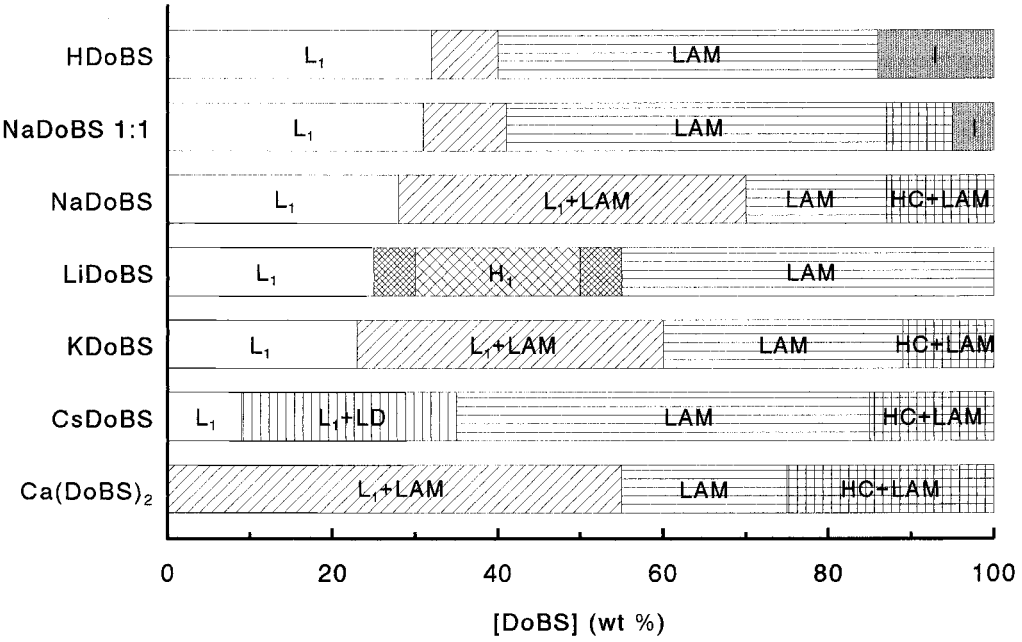

Figure 5. Binary phase diagrams of dodecylbenzenesulfonate with different types of counterions at ambient temperature: unfilled, micellar; horizontal lines, lamellar; hatched, micellar (or water) plus lamellar; crosshatched, hexagonal; double crosshatched, two-phase transition region; vertical lines, lamellar droplets in micellar surroundings; gray, isotropic (plus crystals); crossed, (hydrated) crystals plus lamellar.

phase but which has been reported also for a normal hexagonal phase,[35] has not been observed here. The hexagonal character was also clear from X-ray measurements (see below). At higher concentrations of LiDoBS, a lamellar phase emerges, which is macroscopically recognizable by viscous flow and moderate turbidity. Due to the hygroscopic nature of LiDoBS (see Experimental Section), even the bulk LiDoBS phase appears lamellar.

KDoBS. The lyotropic phase behavior of KDoBS (Figure 6C) is comparable to that of NaDoBS, albeit lamellar units are observed at a lower concentration of KDoBS (23 wt %). The temperature dependence of the lamellar phase boundary (L_1 to L_1 + LAM, see Figure 6C) is reminiscent of the lyotropic phase behavior of CsDoBS.

CsDoBS. With a poorly hydrated Cs^+ as a counterion, the amphiphile will form a lamellar phase at rather low amphiphile concentration at ambient temperature (Figure 6D); at 9 wt % CsDoBS, lamellar units are formed in the micellar solution. In contrast to the lyotropic phase behavior of NaDoBS and KDoBS, these lamellar units are perfectly spherical onion-like aggregates and smaller in size. Moreover, mild flocculation but no coagulation is observed. Figure 3D shows a light microscopy image of this two-phase system at 30 wt % CsDoBS. The spherical lamellar droplets (as large as 5 μm) are clearly distinguished by the Maltese crosses. This birefringence pattern is caused by a radially symmetric stacking of the bilayers. On heating, the lamellar droplets transform into micelles. After cooling down again, the droplets spontaneously reappear. The spontaneous formation of these lamellar droplets (no shear or other type of mechanical energy input is necessary) is quite exceptional.[36] The units apparently profit from the spontaneous curvature of the bilayers. Between 9 and 14 wt % the units do not show a clear birefringence pattern.

Upon increasing CsDoBS concentration, the droplet size increases. At 40 wt % the droplets span the whole sample and henceforth the micellar phase could not be observed anymore. The bulk of the 70 and 80 wt % samples also show the typical birefringence pattern of a lamellar phase. However, a clear liquid phase is present in a minor amount next to the lamellar phase. The structure of this low viscosity phase is at present unknown. The X-ray measurements (see below) reveal a lamellar character with a decreasing repeat distance between 70 and 90 wt % CsDoBS. At the high concentration end (>80 wt %) too little water is present to facilitate a lamellar arrangement for all the amphiphiles; a part remains present as (partially hydrated) crystals next to the lamellar phase.

$Ca(DoBS)_2$. The lyotropic phase behavior of $Ca(DoBS)_2$ hardly varies with temperature (20−90 °C). Only lamellar aggregation is observed, even at very low concentrations (<0.1 wt %). It is unlikely that micelles are formed; only a miniscule amount of monomeric (dissociated) $Ca(DoBS)_2$ will be present in the water phase.[37] The lamellar particles strongly flocculate and coagulate partially to large flakes that easily deform under mild stress. Macroscopically the lamellar phase forms one lump in excess water, which is also ductile but hard to tear into pieces. At higher temperatures, no clearing is observed even at 90 °C in the dilute samples. Between 60 and 80 wt % the lamellar texture spans the whole sample. At higher $Ca(DoBS)_2$ concentrations crystals appear next to the lamellar phase.

Effect of the Third Component: Salt. As discussed in previous papers,[13,14] the addition of salt efficiently induces the lamellar arrangement of NaDoBS molecules, even at low amphiphile concentrations. Here only the water corner of the water/NaDoBS/salt triangle will be sketched, for convenience with orthogonal axes (see Figure 7). In this corner the most interesting phase changes occur. Continuing toward the salt corner (along the *y*-axes of the diagrams), no changes in phase behavior were observed from beyond 1 molal up to the solubility limit of

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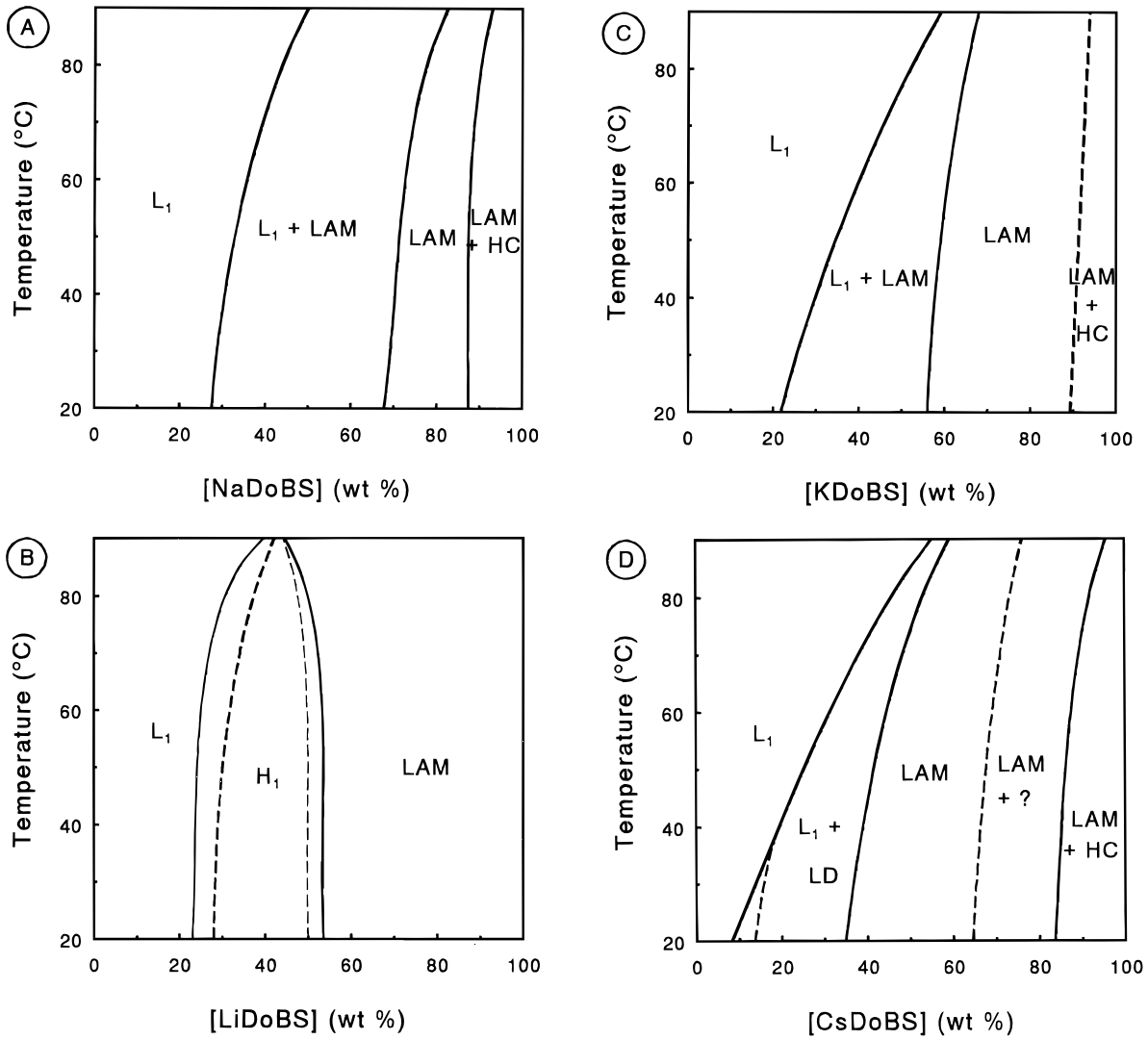

Figure 6. Binary phase diagrams of several DoBS/water systems versus temperature: (A) NaDoBS/water; (B) LiDoBS/water; (C) KDoBS/water; (D) CsDoBS/water. L_1, micellar phase; LAM, lamellar; HC, (hydrated) crystals; H_1, hexagonal; LD, lamellar droplets; W, water.

the salt. The *x*-axes of the diagrams in Figure 7 represent the phase behavior of NaDoBS in water, as is also sketched in Figures 2, 5, and 6A.

The left panel in Figure 7 shows that, in the presence of NaCl, a lamellar arrangement of NaDoBS molecules occurs rather independently of the amphiphile concentration. At somewhat higher salt concentrations, the micellar phase is suppressed efficiently. The straight dashed line in Figure 7A represents the borderline between micellar plus lamellar and only electrolyte solution (W) plus lamellar. The different phases have only been characterized by their macroscopic appearance. The isotropic micellar phase at low salt concentrations has a higher viscosity than the electrolyte solution at higher salt concentrations. Presumably an equilibrium exists between a micellar and a lamellar arrangement of amphiphiles, that slowly shifts toward an all-lamellar arrangement of amphiphiles as the salt concentration increases. Hence, the exact position of this dashed borderline is not known.

In the case of CsCl, as presented in Figure 7B, the same slowly shifting equilibrium toward the lamellar state occurs as in the NaCl case. A remarkable feature of the NaDoBS/water/CsCl phase diagram is the occurrence of an area with lamellar aggregates (spontaneously formed vesicles[11,13]) that are dispersed in the electrolyte solution. As this colloidally fairly stable dispersion spans the whole solution, it is denoted as a one-phase area. The dispersion of lamellar aggregates only occurs at low amphiphile concentration and in the presence of an excess of Cs^+ compared to Na^+ (left of the dotted line in Figure 7B). The border between the dispersion and the two-phase (W + LAM) area is also rather noncooperative and does not represent a phase transition but a stability transition. It is therefore sketched as a dashed curve.

Repeat Distances Measured by X-ray. The different lyotropic liquid-crystalline phases have been well characterized by light microscopy. Important additional evidence was obtained by X-ray diffraction. This technique has been developed for liquid-crystalline phases by Luzatti.[38] It has been elaborately discussed in the literature in relation with the study of liquid crystallinity.[8,39−42]

Figure 8 shows the 1:1 repeat spacings (100 Bragg spacings) of several binary DoBS/water systems in the lamellar state and the 1:1 spacings (10 Bragg spacings)

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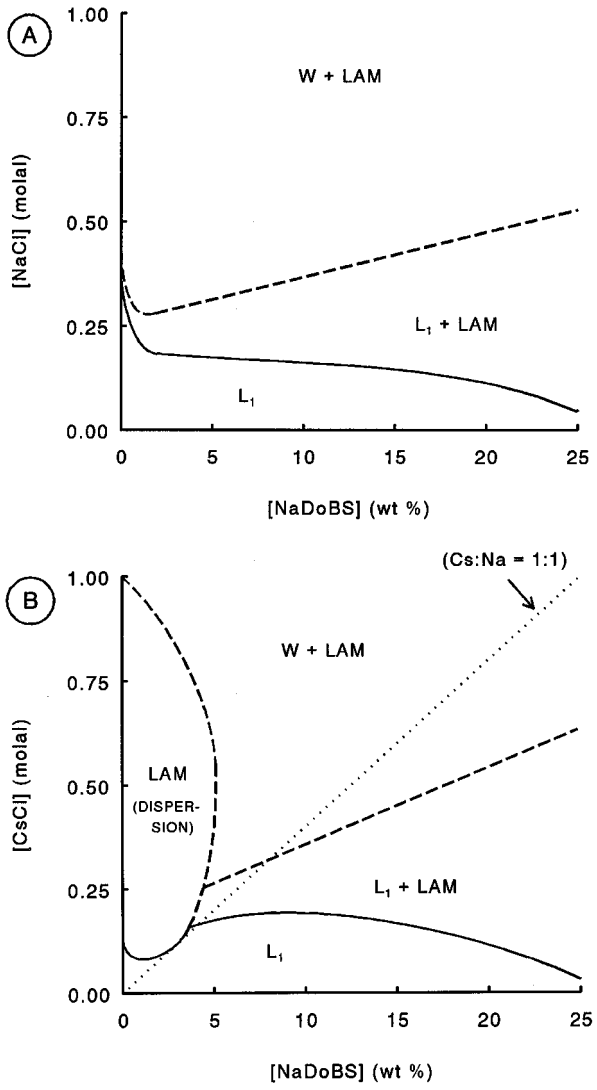

Figure 7. Partial three-component phase diagram of the dilute corner of the water/NaDoBS/salt system. (a) NaCl; (b) CsCl. Notation as in Figure 6.

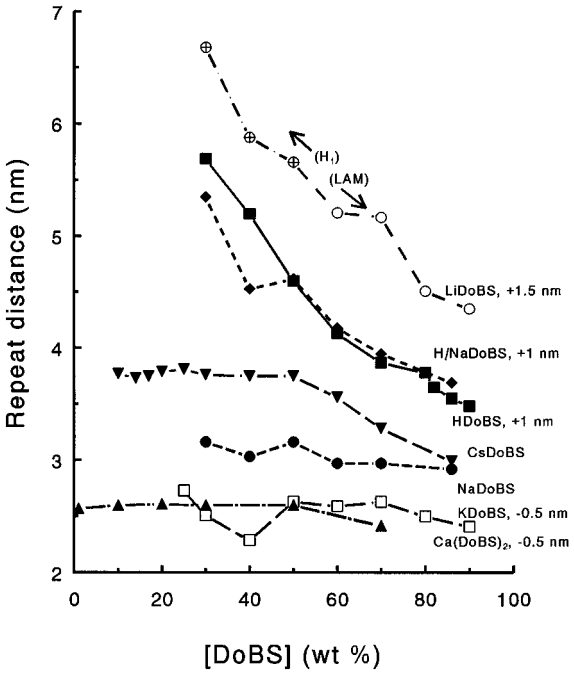

Figure 8. Repeat distances versus composition of binary DoBS/water systems at ambient temperature, measured by X-ray diffraction: ■, HDoBS; ◆, 1:1 H/NaDoBS; ●, NaDoBS; ○, LiDoBS (those filled with crosses represent the H_1 phase); □, KDoBS; ▼, CsDoBS; ▲, $Ca(DoBS)_2$. For clarity the HDoBS and the 1:1 H/NaDoBS curves have been shifted 1 nm upward, the LiDoBS curve has been shifted 1.5 nm upward, and the KDoBS curve and the $Ca(DoBS)_2$ curve has been shifted 0.5 nm downward.

of three binary LiDoBS/water systems in the hexagonal phase. The data in Figure 8 are also compiled in Table 1. Next to the 1:1 spacing, Table 1 also includes higher-order spacings when observed: the 1:2 spacings characteristic for lamellar phases and the $1:\sqrt{3}$ and $1:\sqrt{4}$ spacings typical for hexagonal configurations. The values are in agreement with published data on some metal ion DoBS phases.[43] Attention should be drawn to the 2.65 nm spacing in the 86 wt % HDoBS sample, which is the state with the lowest amount of water needed (three molecules per DoBS amphiphile) to obtain an all-lamellar phase. It illustrates the minimum repeat distance for a lamellar arrangement of HDoBS, not influenced by the size of the counterion (only by three small water molecules). A sample with a lamellar phase next to crystals, such as the 90 wt % NaDoBS binary system, shows lines from the crystalline phase next to the line of the lamellar phase (2.92 nm).

The X-ray measurements for the binary KDoBS and CsDoBS series were severely hampered by the inhomogeneous nature of the samples. Due to the droplet character of the lamellar units in the CsDoBS case, the samples were highly turbid, and much irregular scattering induced the emergence of many different lines. However, the line at about 3.75 nm was present in all samples from 10 to 60 wt % CsDoBS, irrespective of the other lines. This was taken as a reasonable bilayer repeat distance, which means that the lamellar phase is still slightly swollen. At higher CsDoBS concentrations the repeat distance decreases. As mentioned earlier, still a lamellar phase is present that for unknown reasons expels some clear liquid phase. No indication for the occurrence of another lyotropic liquid-crystalline phase has been obtained.

Discussion

Evidently, a simple change in counterion results in drastic differences in lyotropic phase behavior. The hydrophobic moiety of the anionic amphiphile is in all cases the same. The attention is therefore focused on the influence of the counterion, in particular its hydration characteristics and the influence it has on the electrostatics. Apart from the counterion, the overall appearance of the binary phase diagrams is also largely determined by the number of water molecules in action. Noteworthy is the swelling behavior in the HDoBS, the 1:1 Na/HDoBS, and the LiDoBS cases, compared to the nonswelling behavior of NaDoBS, KDoBS, and $Ca(DoBS)_2$ and the limited swelling of CsDoBS. Moreover, LiDoBS is rather unique in forming a hexagonal phase, and CsDoBS is unique in forming a phase where the lamellae prefer a strong and monotonous curvature to form lamellar droplets. $Ca(DoBS)_2$ shows a notoriously stable lamellar arrangement of amphiphiles. These features will now be discussed in relation to their molecular characteristics. Finally a few words will be devoted to the influence of salt on the phase behavior of NaDoBS.

Hydration Features. The amount of water at work dictates the lyotropic status. In Figure 2 it was already unveiled that three water molecules per HDoBS are needed to induce an all-lamellar arrangement for the

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Table 1. Periodicity Measured by X-ray Diffraction for Various Dodecylbenzenesulfonate/Water Samples at Ambient Temperature

composition (wt % DoBS)	water/DoBS ratio[a]	major repeat distance (nm)	phase type[c]
		HDoBS	
40.2	26.7	4.69 (2.35)	LAM
49.9	18.2	4.20 (2.08)	LAM
59.9	12.2	3.60 (1.80)	LAM
69.9	7.8	3.13 (1.57)	LAM
80.0	4.5	2.87 (1.43)	LAM
82.0	4.0	2.78 (1.38)	LAM
85.6	3.0	2.65 (1.32)	LAM
89.8	2.1	2.55[b]	I
90.1	2.0	2.48[b]	I
		H/NaDoBS 1:1	
40.2	27.9	4.34 (2.17)	LAM
49.6	19.1	3.53 (1.76)	LAM
60.6	12.2	3.62 (1.81)	LAM
70.0	8.0	3.18 (1.59)	LAM
79.3	4.9	2.95 (1.48)	LAM
91.0	1.8	2.69[b]	LAM + C
		NaDoBS	
40.6	28.3	3.16 (1.58)	L_1 + LAM
49.3	19.9	3.03 (1.50)	L_1 + LAM
58.4	13.8	3.16 (1.59)	L_1 + LAM
69.9	8.4	2.97 (1.51)	LAM
79.6	5.0	2.97[b]	LAM
89.0	2.3	2.92 (1.47), 3.33, 2.71	LAM + C
		LiDoBS	
30.0	41.5	5.18 (2.92, 2.53)	H_1
40.0	26.7	4.34 (2.52, 2.19)	H_1
49.9	17.9	4.16 (2.41, 1.96)	H_1 + LAM
58.7	12.5	3.71 (1.86)	LAM
69.9	7.7	3.67 (1.85)	LAM
80.1	4.4	3.01 (1.51)	LAM
90.7	1.8	2.85[b]	LAM
		KDoBS	
24.7	60.1	3.23[b]	L_1 + LAM
30.0	46.1	3.01[b]	L_1 + LAM
39.9	29.8	2.79[b]	L_1 + LAM
50.0	19.8	3.13[b]	L_1 + LAM
59.9	13.3	3.09[b]	LAM
69.8	8.6	3.13[b]	LAM
79.9	5.0	3.00[b]	LAM
89.9	2.2	2.91[b]	LAM
		CsDoBS	
10.0	223.5	3.77[b]	L_1 + LD
14.0	153.2	3.73[b]	L_1 + LD
17.0	121.6	3.75[b]	L_1 + LD
20.0	99.5	3.79[b]	L_1 + LD
31.5	57.9	3.81[b]	L_1 + LD
40.1	37.2	3.76[b]	LAM
50.1	24.7	3.75[b]	LAM
58.8	17.4	3.75[b]	LAM
70.3	10.5	3.56 (1.80)	LAM + ?
79.9	6.3	3.28[b]	LAM + ?
89.8	2.8	2.99[b]	LAM + C?
		$Ca(DoBS)_2$	
1.0	1835	3.07[b]	LAM + W
10.0	167.4	3.10[b]	LAM + W
20.2	73.5	3.11 (1.56)	LAM + W
40.0	27.9	3.10 (1.6)	LAM + W
59.7	15.1	3.10 (1.6)	LAM
79.1	4.9	2.92[b]	LAM + C

[a] Number of water molecules per DoBS amphiphile. [b] No higher-order lines observed. [c] LAM, lamellar phase; I, isotropic liquid; C, (hydrated) crystals; L_1, micellar phase; H_1, hexagonal phase; LD, lamellar droplets; ?, unknown; W, water (solution of monomers).

HDoBS amphiphiles. Below this ratio, water molecules are monomerically dispersed in HDoBS, forming an isotropic phase. These water molecules will be tightly bound to the polar headgroups, since the water molecules have such a low self-diffusion that the self-diffusion coefficient (D_w) falls outside the range that can be measured by PGSE NMR.[11] From the combination of the phase diagrams (Figures 2, 5, and 6) and the X-ray diffraction data, listed in Table 1, critical molecular water/amphiphile ratios have been estimated. These are listed in Table 2.

Table 2. Estimated Number of Water Molecules per Single DoBS Amphiphile Associated with a Certain Lyotropic Phase Transition at Ambient Temperature[a]

	I → LAM	C → LAM	LAM → L_1	LAM → H_1	H_1 → L_1
HDoBS	3		35		
H/NaDoBS	<1.5	2−5	41		
NaDoBS		2.5−5	10 → 47		
LiDoBS		<2		18	42−54
KDoBS		2	14 → 70		
CsDoBS		3−6	40 → 225		
$Ca(DoBS)_2$		5 to <15			

[a] For abbreviations of the phases, see Table 1.

Around 10 molecules of water per NaDoBS molecule is the maximum ratio to maintain the lamellar phase as a one-phase system. All additional water is used to create micelles. One part of the surfactant/water mixture will remain as a lamellar phase; another part coexists as a micellar phase. Increasing the water content will further shift this equilibrium to the micellar phase that occurs around 29 wt % (47 molecules of water per NaDoBS molecule). Such a phenomenon also occurs in the binary KDoBS/water system between 23 and 60 wt % and the binary CsDoBS/water system between 9 and about 40 wt %.

It is remarkable that the hydration characteristics of the cations that dominate the amphiphile behavior in dilute aqueous surroundings.[13] at first sight do not correlate with the numbers in Table 2. Here Li^+ is already satisfied with a small amount of water to induce a lamellar arrangement of amphiphiles, whereas Cs^+ is much more demanding. To induce a lamellar arrangement, approximately 2−6 water molecules are needed per amphiphile, irrespective of the type of cation. Such a number has been found for other systems as well.[21,44] Toward the dilute side of the binary systems an inverse relation applies: a counterion that binds poorly is also better hydrated in excess water. Hence stronger electrical double-layer repulsions occur when an ion binds poorly and the transition to a micellar phase occurs at higher surfactant concentration, or it even allows for the occurrence of a hexagonal phase, as will be discussed later.

Swelling. The driving force for the swelling of a lamellar phase is a long-range repulsion between the bilayers that is larger than the long-range attraction. In the literature much attention has been paid to undulations as the driving force for extreme swelling.[7,45−50] Also electrostatics often play a role, which, in addition, is found to be able to enhance the undulation repulsion.[51] The undulation repulsion depends on the bending rigidity (flexibility) of the bilayer sheet. The rigidity of the hydrophobic core is an important factor in undulations. Bilayers that consist of DoBS amphiphiles are rather thin (estimated thickness of 1.9 nm[12]) and therefore will be

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rather flexible. This cannot explain the swelling in one case and the nonswelling in the other; as in all systems the same DoBS amphiphiles are used. The other important factor that allows highly undulating bilayers is a low surface charge density.[46,47] A low surface charge density in bilayer systems composed of ionic amphiphiles is only obtained for a high counterion binding, which is especially found for cations such as K^+, Cs^+, Ca^{2+}, and to a minor extent Na^+. And these are exactly the systems that hardly swell or not at all.

Hence it is proposed that the swelling in the HDoBS, 1:1 Na/HDoBS, and LiDoBS cases is caused by a low counterion binding. This leads to an effective surface charge and therefore to an increased electrostatic repulsion. Note, however, that an increase in surface charge density will also increase the bilayer rigidity and hence decrease the undulation force, thereby decreasing this contribution to the swelling. The extreme swelling observed for DDAB (didodecyldimethylammonium bromide) has also been couched in terms of electrostatic effects.[52] The electrical double-layer repulsions cause swelling by osmosis rather than by electrostatic repulsions:[15] the dissociated counterions and the headgroups, whose charges are relatively poorly compensated by counterion binding, need much water for hydration. All the added water will be harnessed to swell the interlamellar water layer.

When the long-range attractions outweigh the long-range repulsions, swelling is blocked. This situation can be caused by several factors. One involves the notion that for a high counterion binding the electrical double-layer repulsion is weak. Also a larger van der Waals attraction might occur between bilayers with a high counterion binding, particularly when the atomic mass and thus the polarizability of the counterion is high (as with, for instance, cesium).

Multivalent ions such as Ca^{2+} are effective in screening the electrical double-layer repulsions. Moreover, an additional ion−ion correlation attraction is said to occur,[15,18] resulting in a large interbilayer attraction. Hence the bilayer repeat distance is small, and the lamellar arrangement persists to even very low concentrations of $Ca(DoBS)_2$. Such a special interbilayer attraction caused by a specific Na^+−headgroup interaction has even been proposed for the lamellar phase that occurs for the isomerically pure 4/7 NaDoBS.[7] Extending this ion−ion correlation attraction to the CsDoBS case is too speculative, although no other explanation appears to be on hand for the expulsion of a clear aqueous phase from the CsDoBS lamellar phase at higher amphiphile concentrations.

LiDoBS Hexagonal Phase. The highly hydrated Li^+ binds poorly to negatively charged surfaces. The swelling behavior is comparable to that of HDoBS, another amphiphile with a small, poorly binding and highly hydrated counterion. However, LiDoBS forms a hexagonal phase, in contrast to HDoBS. This hexagonal phase also swells, or the rod−rod distance increases as the water content increases.

The formation of cylindrical aggregates that arrange in a hexagonal fashion is the result of a rather high electrostatic repulsion between the headgroups due to the low Li^+ counterion binding, as compared to NaDoBS. As a consequence, the headgroup−headgroup distances are larger, just large enough to allow the formation of rods that prefer a hexagonal arrangement. On further dilution with water, the hexagonal phase turns into a micellar phase, most likely with wormlike micelles.

Usually a narrow band of a cubic phase (most often with the space group *Ia3d*) separates the hexagonal and the lamellar phases.[6,8−10] This cubic phase is viewed as a transition between cylinders and planes.[53,54] A first-order transition between a (normal) hexagonal and a lamellar phase is, however, not uncommon.[55] When a surfactant displays both hexagonal and lamellar phases, the intermediate cubic phase can easily be inferred from contact experiments with the use of a light microscope with crossed polarizers. When bulk surfactant is contacted with water, the cubic phase clearly appears as a dark (optically isotropic) band between the hexagonal and the lamellar phases.[6,56−58] Such a cubic phase has not been detected for LiDoBS. In a contact experiment, the hexagonal phase is seen to grow straight from the lamellar phase. On heating the 50 wt % sample (by a hot stage, simultaneously observing the sample by a light microscope, see Experimental Section), the hexagonal patches melt off into dark (apparently isotropic) areas, in which at still higher temperatures a lamellar texture grows.[27] Hence a cubic texture cannot be ruled out (at higher temperatures), but no conclusive evidence exists. The X-ray diffractogram of the 50 wt % LiDoBS sample clearly showed the $1:\sqrt{3}:\sqrt{4}$ pattern, although the $\sqrt{4}$ line was relatively large and could as well be partially the second-order reflection of the lamellar phase (1:2) or (less likely) even of the cubic phase.

The CsDoBS Lamellar Droplets. In comparison with the lamellar units found in the micellar plus lamellar two-phase system of NaDoBS, CsDoBS forms clearly *spherical* lamellar units, spherulites, "onions", or here called lamellar droplets (see also the difference between the birefringent units of Figure 3B and D). The strong and monotonous curvature and the only mild flocculation with preservation of the spherical character of the droplets point to a special type of lamellar phase. Some more details are noteworthy:

(i) The lamellar droplets are formed in a binary system (CsDoBS and water), in the literature only described for the AOT/water system (Aerosol OT, sodium bis(2-ethylhexyl) sulfosuccinate[26,36]), where lamellar droplets form spontaneously from the micellar phase upon cooling. For dilute binary DDAB/water systems lamellar droplets have been observed, although shear has been applied to obtain the dispersion.[52] Other reports in the literature describe lamellar droplets which only occur in multiple-component systems (surfactant/cosurfactant/water(/salt)).[12,59,60]

(ii) The lamellar droplets coexist with a micellar phase.

(iii) Although the phases have been homogenized by thorough teasing (shaking and sonication (see Experimental Section), which means much energy input), the droplet character remains even after months. It is apparently a state of low Gibbs energy.

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(iv) The temperature where the lamellar droplets disappear in favor of the micellar phase depends strongly on the amount of amphiphile, in contrast with a virtual absence of a temperature dependence for the lamellar to micellar transition for the other binary systems (see Figure 6).

(v) After cooling down from the micellar state, the lamellar droplets spontaneously reappear, without the need for applying extra energy (such as by shear or sonication). The droplets slowly grow in size. This spontaneous growth of spheres also occurs in the 40 wt % CsDoBS system after it has been heated up to the micellar phase and subsequently cooled down.

(vi) Hence, at 40 wt % (or higher) the state of lamellar droplets continues, hampered, however, by the overlap of the growing spheres.

(vii) The repeat distance (see Table 1) is rather independent of composition; from 10−60 wt % CsDoBS it is about 3.75 nm. The hydrophobic core is estimated to be about 1.9 nm thick,[12] leaving still a relatively large 1.85 nm as an equilibrium distance for the headgroups, the counterions, and a relatively large amount water, indicating a limited swelling. This minor swelling has been explained for DDAB by an osmotic effect, since the micellar phase and the lamellar phase are in equilibrium and so are the osmotic pressures of both phases. If the lamellar phase would swell further, it would compress the micellar phase. The resistance of the micelles to this effect hampers the swelling of the lamellar phase.[52]

(viii) The largest droplets are about 5 μm in diameter, which comes down to maximally about 600 bilayers. It is not clear what exactly is the structure of the inner part of the droplet, but presumably, going toward the center of the droplet, at a certain point the curvature imposed on the bilayer becomes unacceptable, and henceforth only a water pool exists (or a pool containing a micellar phase).

(ix) The occurrence of this phase behavior is related to the characteristics of the Cs^+ counterion: high counterion binding, little electrostatic repulsion between the headgroups, a low electrical double-layer repulsion between the bilayers, little hydration, and a relatively strong van der Waals attraction.

All these arguments illustrate the exceptional status of the dispersion of lamellar droplets in a micellar phase. The Gaussian bending modulus (k_G, introduced by Helfrich[61]) could be estimated as negative, thereby granting spontaneous curvature.[39,62] Why would a bilayer profit from spontaneous curvature? When the bilayer remains flat, the amphiphiles might be forced in a frustrated packing regime. To account for this frustration, the bilayer can deform either by stretching or by bending. This last option is energetically less costly.[39,63] The difficult counterion binding inside the sphere will be more than compensated by a good counterion binding on the outside. In order to accomodate a large counterion such as Cs^+ close to the headgroups (at a low degree of dissociation), the packing of amphiphiles in the bilayer might become frustrated. This could be the driving force for the formation of vesicles which serve as nuclei of the lamellar droplets.

The spontaneous curvature is particularly important for the bilayers in the center of the droplet. These bilayers are formed first upon cooling down a micellar solution. In this initial stage the topology of the bilayer is still important. Once several of those highly curved bilayers have formed, they act as a nucleus on which new bilayers can be formed, causing the growth of the droplet. Now the attraction between the bilayers becomes more important than the topology as the driving force for the formation of lamellar droplets, because the curvature decreases going toward the outer bilayers.

$Ca(DoBS)_2$ Lamellar Phase. Calcium salts of anionic surfactants usually have high Krafft temperatures.[64,65] Hence only at higher temperatures can the amphiphile be released from its crystal lattice to form micelles in aqueous surroundings. $Ca(DoBS)_2$ preferentially forms a lyotropic lamellar arrangement rather than a crystal in aqueous surroundings, even at high dilution. The strong Ca^{2+} binding to the surface of a DoBS aggregate reduces electrostatic repulsions between the headgroups efficiently. Moreover, the strong interbilayer attraction prevents swelling (see above). Water is not able to break down the lamellar structure into a micellar phase (neither is the temperature), although it is able to hydrate $Ca(DoBS)_2$ to provide a lamellar phase. Macroscopically the $Ca(DoBS)_2$ lamellar phase has a peculiar nature, induced by an apparant strong lateral adhesion (as in graphite) next to the large interbilayer attraction. (The use of lyotropic lamellar phases as lubricants has recently been proposed.[66]) As the amount of water decreases to below the amount where all the amphiphile can be hydrated to form a lamellar phase, part of the amphiphile crystallizes, instead of forming an inverse hexagonal arrangement, as is common for calcium ion amphiphiles.[34,39]

Influence of Salt. Salt is much more efficient in inducing the lamellar arrangement of NaDoBS than the amphiphile itself by varying its concentration. Over a concentration region of 5−20 wt % NaDoBS, only about 0.2 molal of salt (both NaCl and CsCl) is sufficient. This illustrates the importance of regulating the electrical double-layer interactions by the addition of salt. Higher electrolyte concentrations will force NaDoBS completely into a lamellar arrangement and disfavor micellar aggregation.[11,13,14]

Remarkable is that CsCl induces the spontaneous formation of a colloidally rather stable dispersion of lamellar aggregates at low amphiphile concentration, as has been elaborately discussed before.[13] Similar to the remarkable lyotropic phase behavior of CsDoBS, the special behavior can be explained by the high counterion binding capacity of Cs^+. The dispersion of lamellar aggregates typically occurs at an excess of Cs^+ relative to Na^+, where it deprives the DoBS aggregates from Na^+. The transition from the area with a dispersion of lamellar aggregates into the area with a lamellar phase in water (the curved dashed line in Figure 7B) is a transition in colloidal stability rather than a phase transition.

The salt concentration in the interlamellar water layers is lower than that in the continuous electrolyte solution.[12] The salt-induced lamellar phase appears as unhandy, strongly flocculated lamellar units. In order to obtain better dispersions of lamellar units, as is needed for commercial products, a nonionic surfactant could be applied and/or polymers could be added that modify the morphology and the colloidal stability of the lamellar phase.[12]

Conclusions

The lyotropic phase behavior of several dodecylbenzenesulfonates is strongly influenced by the type of counterion and the relative amount of water. About 2−6 water

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molecules per amphiphile are needed to induce the lamellar arrangement of amphiphiles. Typical are the differences in swelling behavior for the several counterions, which are related to the counterion binding capacity:

(i) Low counterion binding for highly hydrated ions leads to a large electrical double-layer repulsion between the bilayers and hence to large swelling.

(ii) Low counterion binding leads to high hydration needs ("thirsty" counterions).

(iii) High counterion binding causes low electrical double-layer repulsion but causes, moreover, an increased van der Waals attraction because of the higher atomic mass of the well-bound counterions, leading to little or no swelling.

(iv) Additional ion−ion correlations apply in certain cases.

The hexagonal phase that occurs in the binary LiDoBS/water system is a result of the low counterion binding of Li^+. The concomitantly large headgroup−headgroup repulsion leads to a balanced headgroup-headgroup distance that allows for the packing in cylindrical aggregates, arranged in a hexagonal fashion.

The formation of lamellar droplets in the binary CsDoBS/water system might be explained by a "frustrated" packing that is due to the large size of the Cs^+ ion. To overcome this frustration, the bilayers curve rather than stretch laterally, because the latter option costs more Gibbs energy.

The lyotropic phase behavior of KDoBS is between that of NaDoBS and CsDoBS.

$Ca(DoBS)_2$ forms a lamellar phase that covers a large part of the phase diagram, without a coexisting micellar phase. The absence of swelling is due to a high interbilayer attraction that can be explained in terms of the efficient counterion binding capacity of Ca^{2+}, and in addition, ion−ion correlations might cause extra attractive interactions.

Salt is efficient in inducing lyotropic lamellar order in ternary NaDoBS/water/salt systems.

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